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SYNTHESIS AND CHARACTERIZATION OF ALUMINUM-PHOSPHORUS ADDUCTS: X-RAY CRYSTAL STRUCTURES OF  $\text{Cl}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$  AND  $\text{Br}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$ 

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The attempted dehalosilylation reactions between  $\text{AlX}_3$  ( $\text{X} = \text{Cl}, \text{Br}$ ) and  $\text{P}(\text{SiMe}_3)_3$  in toluene in 1:1 mole ratios afforded only the adducts  $\text{Cl}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  (I) and  $\text{Br}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  (II), respectively. Compounds I and II were characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{27}\text{Al}$ , and  $^{31}\text{P}$  solution NMR spectroscopy, as well as partial elemental analysis. In addition, the solid state structures of the toluene solvates of I and II were determined by single-crystal X-ray analysis. Characterization revealed that the solid solvated adducts I and II are isostructural and their crystals are isomorphous. In each compound, the Al and the P atoms reside in tetrahedral environments, with each  $\text{X}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  ( $\text{X} = \text{Cl}, \text{Br}$ ) molecule associated with one interstitial toluene molecule in the crystals. These adducts are noteworthy in that they possess extremely short, essentially equal Al-P bond lengths [For I:  $\text{Al}-\text{P} = 2.392(4) \text{ \AA}$ , and for II:  $\text{Al}-\text{P} = 2.391(6) \text{ \AA}$ ], which are the shortest found to date in aluminum-phosphorus molecular species.

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 $\text{Cl}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$  AND  $\text{Br}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$**

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**Abstract** - The attempted dehalosilylation reactions between  $\text{AlX}_3$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) and  $\text{P}(\text{SiMe}_3)_3$  in toluene in 1:1 mole ratios afforded only the adducts  $\text{Cl}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  (I) and  $\text{Br}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  (II), respectively. Compounds I and II were characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{27}\text{Al}$ , and  $^{31}\text{P}$  solution NMR spectroscopy, as well as partial elemental analysis. In addition, the solid state structures of the toluene solvates of I and II were determined by single-crystal X-ray analysis. Characterization revealed that the solid solvated adducts I and II are isostructural and their crystals are isomorphous. In each compound, the Al and the P atoms reside in tetrahedral environments, with each  $\text{X}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  ( $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) molecule associated with one interstitial toluene molecule in the crystals. These adducts are noteworthy in that they possess extremely short, essentially equal Al-P bond lengths [For I:  $\text{Al}-\text{P} = 2.392(4) \text{ \AA}$ , and for II:  $\text{Al}-\text{P} = 2.391(6) \text{ \AA}$ ], which are the shortest found to date in aluminum-phosphorus molecular species.

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Recent investigations in our laboratory have focused on the synthesis of novel compounds which may serve as single-source precursors to a variety of III-V electronic materials. It has been found that dehalosilylation reactions between tris(trimethylsilyl)arsine or phosphine and an alkyl group III halide or group III trihalide offer facile routes to the preparation of compounds containing the desired III-V bond.<sup>1</sup> The success of this synthetic method has led to the isolation of numerous compounds containing both  $\overline{\text{MEME}}$  ( $\text{M} = \text{Ga}$ ,  $\text{E} = \text{As}$ ;<sup>2-5</sup>  $\text{M} = \text{In}$ ,  $\text{E} = \text{P}^6$  or  $\text{As}$ ;<sup>7</sup>) and  $\overline{\text{MEMCl}}$  ( $\text{M} = \text{Ga}$ ,  $\text{E} = \text{As}$ ;<sup>2,4,5</sup> or  $\text{P}$ ;<sup>8</sup>  $\text{M} = \text{In}$ ,  $\text{E} = \text{P}^6$  or  $\text{As}$ ;<sup>8</sup>) cores. In a variety of heavier III-V systems, we have also isolated numerous 1:1 adducts of the types  $\text{R}_3\text{M}\cdot\text{E}(\text{SiMe}_3)_3$  ( $\text{R} = \text{Ph}$ ,  $\text{M} = \text{Ga}$ ,  $\text{E} = \text{As}$ <sup>9</sup> or  $\text{P}$ ;<sup>10</sup>  $\text{R} = \text{Me}_3\text{SiCH}_2$ ,  $\text{M} = \text{In}$ ,  $\text{E} = \text{As}$ ;<sup>9</sup>  $\text{R} = \text{C}_6\text{F}_5$ ,  $\text{M} = \text{Ga}$ ,  $\text{E} = \text{As}$ <sup>11</sup>),  $\text{R}_2(\text{X})\text{M}\cdot\text{E}(\text{SiMe}_3)_3$  ( $\text{R} = i\text{-Bu}$ ,  $\text{X} = \text{Cl}$ ,  $\text{M} = \text{Al}$ ,  $\text{E} = \text{As}$ ;<sup>12</sup>  $\text{R} = \text{Ph}$ ,  $\text{X} = \text{Cl}$ ,  $\text{M} = \text{Ga}$ ,  $\text{E} = \text{P}$ <sup>10</sup>), and  $\text{X}_3\text{M}\cdot\text{E}(\text{SiMe}_3)_3$  ( $\text{X} = \text{Cl}$ ,  $\text{M} = \text{Al}$ ,  $\text{E} = \text{As}$ ;<sup>13</sup>  $\text{X} = \text{I}$ ,  $\text{M} = \text{Ga}$ ,  $\text{E} = \text{As}$ <sup>14</sup>) from attempted dehalosilylation reactions. More recently, we reported the isolation of the adducts  $\text{Et}_2(\text{Cl})\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$ ,  $\text{Et}(\text{Cl})_2\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$ , and  $i\text{-Bu}_2(\text{Cl})\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$  from similar reactions between alkylaluminum halides and  $\text{P}(\text{SiMe}_3)_3$ .<sup>15</sup> As a continuation of our investigation into the chemistry of the aluminum-phosphorus system, we report herein the synthesis and structural characterization of the adducts  $\text{Cl}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$  (I), and  $\text{Br}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$  (II).

## EXPERIMENTAL

### Synthesis

All manipulations were performed using standard Schlenk vacuum techniques or in a Vacuum Atmospheres HE-493 Dri-Lab under an argon atmosphere. Solvents, including those used for NMR spectra, were appropriately dried and distilled under dry nitrogen prior to use.  $\text{AlCl}_3$  and  $\text{AlBr}_3$  were purchased from Aldrich Chemical Co., Inc., Milwaukee, WI, and purified by sublimation.  $\text{P}(\text{SiMe}_3)_3$  was prepared *via* procedures by Becker

*et al.*<sup>16</sup>  $^1\text{H}$  and  $^{13}\text{C}$  ( $^1\text{H}$ ) NMR spectra were obtained on a Varian XL-300 at 300.0 and 75.4 MHz, respectively, and were referenced to TMS via the residual protons or carbons of  $\text{C}_6\text{D}_6$ .  $^{27}\text{Al}$  and  $^{31}\text{P}$  ( $^1\text{H}$ ) NMR spectra were obtained on a Varian Unity 500 NMR at 130.2 and 202.3 MHz, respectively, and were externally referenced to  $\text{H}_3\text{PO}_4$  and  $\text{Al}(\text{NO}_3)_3$ , both at  $\delta$  0.00 ppm. Melting points (uncorrected) were taken in sealed capillaries on a Thomas Hoover Uni-melt apparatus. Elemental Analyses were performed by E+R Microanalytical Laboratory, Inc., Corona, NY. Single-crystal data for I were collected at the Crystal Structure Center, Duke University, on an Enraf-Nonius CAD-4 diffractometer, at room temperature, with graphite-monochromated  $\text{Cu-K}\alpha$  radiation, and those for II were collected at the University of North Carolina, on a Rigaku AFC6/S diffractometer at  $-170^\circ\text{C}$ , with graphite-monochromated  $\text{Mo-K}\alpha$  radiation.

#### $\text{Cl}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$ (I)

Inside the dry-box, a one-necked screw-top  $250\text{ cm}^3$  round-bottomed flask, equipped with a Teflon valve and stir-bar, was charged with  $\text{AlCl}_3$  (0.3381 g, 2.536 mmol) and toluene ( $40\text{ cm}^3$ ), forming a bright yellow solution. To this was added  $\text{P}(\text{SiMe}_3)_3$  (0.6353 g, 2.536 mmol) in toluene ( $40\text{ cm}^3$ ), resulting in the immediate loss of yellow colour to give a clear, colorless liquid. The flask was placed in an ultrasonic cleaning bath for 48 h, during which a temperature of  $45^\circ\text{C}$  was reached. During sonication no change in the appearance of the solution was observed. However, upon slow cooling to room temperature, large colourless solvated X-ray diffraction quality crystals of I formed. Toluene was removed from the product by evacuation at  $25^\circ\text{C}$  for 2 h to yield a white crystalline solid; 0.412 g, 71.5% yield; no m.p. observed up to  $300^\circ\text{C}$ . Found: C, 28.06; H, 6.96; Al, 7.31; Cl, 27.59; P, 7.99%. Calc. for  $\text{C}_9\text{H}_{27}\text{AlCl}_3\text{PSi}_3$ : C, 28.16; H, 7.10; Al, 7.10; Cl, 27.70; P, 8.07%.  $^1\text{H}$  NMR:  $\delta$  0.34 (d, 27 H,  $\text{SiMe}_3$

$[J_{\text{P-H}} = 5.61 \text{ Hz}]$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  3.07 (d,  $\text{SiMe}_3$  [ $J_{\text{P-C}} = 8.1 \text{ Hz}$ ]).  $^{27}\text{Al}$  NMR:  $\delta$  117.86 (s).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  -240.25 (s).

## $\text{Br}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$ (II)

In a manner similar to that employed for the preparation of I,  $\text{AlBr}_3$  (0.2684 g, 1.006 mmol) was dissolved in toluene (30  $\text{cm}^3$ ), furnishing a clear, yellow-orange solution.  $\text{P}(\text{SiMe}_3)_3$  (0.252 g, 1.006 mmol) in toluene (30  $\text{cm}^3$ ) was added, resulting in a clear, colourless liquid. The flask containing the liquid was immersed in an ultrasonic cleaning bath at 45  $^\circ\text{C}$  for 48 h. Upon removal from the bath and cooling to 0  $^\circ\text{C}$  for several days, large solvated X-ray quality crystals of II formed in solution. Single crystals of II suitable for X-ray crystallographic analysis were harvested from the flask. The volatiles were then removed *in vacuo* to yield an off-white solid product, which was washed with pentane (10  $\text{cm}^3$ ) and dried to give a white crystalline solid; 0.491 g, 63.3% yield; no m.p. observed up to 300  $^\circ\text{C}$ , turns gray at 290  $^\circ\text{C}$ . Found: C, 20.73; H, 5.08; Al, 5.11; Br, 46.50; P, 5.95%. Calc. for  $\text{C}_9\text{H}_{27}\text{AlBr}_3\text{PSi}_3$ : C, 20.90; H, 5.27; Al, 5.22; Br, 46.34; P, 5.99%.  $^1\text{H}$  NMR:  $\delta$  0.33 (d, 27H,  $\text{SiMe}_3$  [ $J_{\text{P-H}} = 5.61 \text{ Hz}$ ]).  $^{13}\text{C}\{^1\text{H}\}$  NMR:  $\delta$  3.15 (d,  $\text{SiMe}_3$  [ $J_{\text{P-C}} = 8.0 \text{ Hz}$ ]).  $^{27}\text{Al}$  NMR:  $\delta$  102.16 (s).  $^{31}\text{P}\{^1\text{H}\}$  NMR:  $\delta$  -218.91 (s).

## *X-ray structural solution and refinement*

Crystallographic data for I and II are summarized in Table I. A colourless crystal of I was mounted inside a flame-sealed 0.6 mm thin-walled glass capillary under an inert argon atmosphere. Preliminary unit-cell parameters and space group information were obtained from oscillation and precession photographs. The orthorhombic space group *Pbca* was established by the Laue symmetry and systematic absences. X-ray intensity data

were recorded at 25 °C (Cu-K $\alpha$  radiation,  $\lambda = 1.5418 \text{ \AA}$ , graphite monochromator). Refined unit-cell parameters were derived from the diffractometer setting angles for 25 reflections ( $35^\circ < \theta < 40^\circ$ ) widely separated in reciprocal space. Intensity data (+*h*, +*k*, +*l*; 4807 reflections,  $\theta_{\text{max}} = 67^\circ$ ) were corrected for the usual Lorentz and polarization effects; an empirical absorption correction (derived from  $\psi$ -scans) was also applied. A total of 1674 reflections, with  $I > 3.0\sigma(I)$ , were retained for the analyses. The final atomic positional parameters of the isomorphous and isostructural As analog<sup>13</sup> were used as initial input to the structure-factor calculations. Several rounds of full-matrix least-squares adjustment of positional and thermal parameters of these atoms (at first isotropic, then anisotropic) followed. During the course of these iterations, the parameters of the toluene carbon atoms refined to physically unacceptable values and so these atoms were constrained to have isotropic thermal parameters in the subsequent least-squares cycles. In the final iterations, hydrogen atoms, except those of the toluene methyl group, were incorporated at their calculated positions (C—H = 1.05 Å) and an extinction correction was included as a variable. The parameter refinement converged at  $R = 0.061$  ( $R_w = 0.088$ ). A final difference Fourier synthesis contained no unusual features [max.  $\Delta\rho$  ( $\text{e \AA}^{-3}$ ): 0.77]. An ORTEP<sup>17</sup> diagram showing the solid-state structure and atom labeling scheme of I is presented in Fig. 1. Selected bond lengths and bond angles are listed in Table 2. Crystallographic calculations were performed on PDP11/44 and MicroVAX computers by use of the Enraf-Nonius Structure Determination Package (SDP).<sup>18</sup> For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref 19. In the least-squares iterations,  $\Sigma w\Delta^2$  [ $w = 1/\sigma^2(|F_o|)$ ,  $\Delta = (|F_o| - |F_c|)$ ] was minimized.

For compound II, a single crystal was affixed to the end of a glass fiber using a viscous oil under an inert nitrogen atmosphere, then transferred to a goniometer head and cooled to -170°C under a flow of nitrogen. X-ray intensity data were recorded using the  $\omega$  scan mode (Mo-K $\alpha$  radiation,  $\lambda = 0.71073 \text{ \AA}$ ). Cell parameters and an orientation matrix



corresponded to an orthorhombic cell, space group *Pbca* for **II**. The structure of **II** was solved by direct methods. Refined unit-cell parameters were derived from the diffractometer setting angles for 55 reflections ( $30^\circ < 2\theta < 40^\circ$ ). Intensity data ( $+h, +k, +l$ ; 3566 reflections,  $\theta_{\max} = 45^\circ$ ) were corrected for absorption using  $\psi$ -scans. Full-matrix least-squares adjustment of positional and thermal parameters of these atoms was applied, in which the last least-squares cycle was calculated with 59 atoms, 217 parameters, and 1522 [with  $I > 2.5\sigma(I)$ ] out of the 3566 reflections. In the final iterations, hydrogen atoms, except those of the toluene methyl group, were incorporated at their calculated positions ( $C-H = 0.96 \text{ \AA}$ ) using a riding model, with parameter refinement converging at  $R = 0.052$  ( $R_w = 0.050$ ). A final difference-Fourier synthesis revealed no unusual features [max.  $\Delta\rho$  ( $e \text{ \AA}^{-3}$ ): 0.64]. An ORTEP<sup>17</sup> diagram showing the solid-state structure and atom labeling scheme of **II** is illustrated in Fig. 2, and selected bond lengths and bond angles are listed in Table 2. Crystallographic calculations were performed on a DEC 3000/400 computer using the NRCVAX suite of structure determination programs.<sup>20</sup> For all structure-factor calculations, neutral atom scattering factors and their anomalous dispersion corrections were taken from ref 19.

Supplementary material: atomic coordinates, thermal parameters, bond lengths and angles and crystallographic data have been deposited with the Cambridge Crystallographic Data Centre.

## RESULTS AND DISCUSSION

Of late, the focus of our laboratory has been the development of facile methods of preparing compounds which may function as possible precursors to electronic materials due to the presence of III-V covalent bonds.<sup>1</sup> To this end, dehalosilylation reactions have been successfully applied to many of the III-V systems.<sup>11,13,14,21</sup> Our investigations have shown that such reactions between heavier group III metal trihalides and

tris(trimethylsilyl)arsine in a 1:1 mole ratio proceed directly to the formation of the metal arsenide, with the concomitant elimination of trimethylsilyl halide (Eqn. 1).<sup>13</sup> However,



M = Ga, X = Cl or Br

M = In, X = Cl

the analogous reaction between  $\text{AlCl}_3$  and  $\text{As}(\text{SiMe}_3)_3$  affords the solvated adduct,  $\text{Cl}_3\text{Al}\cdot\text{As}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$  (**III**)<sup>13</sup> rather than the expected dehalosilylation product. Toluene is removed from **III** under vacuum at 25 °C, and further heating then generates AlAs with the simultaneous elimination of  $\text{Me}_3\text{SiCl}$ .

In like manner to the attempted dehalosilylation reaction in the Al-As system, reactions between the heavier group III trihalides and tris(trimethylsilyl)phosphine also fail to undergo complete dehalosilylation to form metal phosphides. Instead, reactions of  $\text{P}(\text{SiMe}_3)_3$  with  $\text{MX}_3$  (M = Ga, X = Cl or Br;<sup>10,22</sup> M = In, X = Cl<sup>23</sup>) yield characterizable oligomeric intermediates, which must be heated to high temperatures in order to eliminate 100% of the trimethylsilyl halide and form the III-V binary materials. In order to further study the nature of this synthetic pathway, dehalosilylation reactions were investigated in the aluminum-phosphorus system wherein aluminum trihalides were reacted with tris(trimethylsilyl)phosphine in order to form compounds which might possess the desired Al—P covalent bond. We find that the attempted Al-P dehalosilylation reactions proceed in a manner similar to both the Al-As system and the aforementioned group III-phosphorus systems. Herein, we report the synthesis and crystal structures of  $\text{Cl}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$  (**I**) and  $\text{Br}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$  (**II**).

Reaction of  $\text{P}(\text{SiMe}_3)_3$  with  $\text{AlX}_3$  (X = Cl, Br) in a 1:1 mole ratio in toluene afforded the solvated adducts **I** and **II**, respectively. The ORTEP<sup>17</sup> diagrams of the solid-state conformations of both **I** and **II** are individually shown in Figs. 1 and 2; selected

bond lengths and angles are provided in Table 2. Compounds **I** and **II** are isostructural with the aforementioned solvated Al-As adduct,  $\text{Cl}_3\text{Al}\cdot\text{As}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$  (**III**)<sup>13</sup>, and the solvated crystals are isomorphous, crystallizing in the orthorhombic space group *Pbca*. Structural data show that **I** and **II** each contain an Al—P bond lying on a three-fold rotation axis, with the Al and P substituents in a somewhat staggered conformation. The bonds radiating from the Al and P atoms in **I** are rotated by a mean angle of  $42.4^\circ$  from an eclipsed position, which is nearly identical to the conformation around the Al-As bond in **III**, where the value is  $42.7^\circ$ .<sup>13</sup> The analogous bonds in **II** are also staggered by an average rotation of  $44.2^\circ$ .

In the chloro analogs **I** and **III**, both the Al and P centers are four-coordinate and reside in nearly tetrahedral environments. As is predicted by the Valence Shell Electron Pair Repulsion (VSEPR) model,<sup>24,25</sup> the P—Al—Cl bond angles in **I** are slightly less than tetrahedral, ranging from  $107.8(1)$  to  $108.4(2)^\circ$ , as is the case in **III**, where the As—Al—Cl angles fall between  $107.7(1)$  and  $107.9(1)^\circ$ .<sup>13</sup> It is also noted that the Cl—Al—Cl angles are in adducts **I** and **III** [ $110.5(2)$ - $111.4(2)^\circ$  for **I** and  $110.0(1)$ - $111.6(1)^\circ$  for **III**], all greater than tetrahedral, are markedly similar, suggesting that the change in donor strength between  $\text{P}(\text{SiMe}_3)_3$  and  $\text{As}(\text{SiMe}_3)_3$  has a relatively small affect on the geometrical environment around the Al atom.

Similarities in bond angles are also present in the coordination spheres around the P and the As atoms of **I** and **III**, respectively. The Al—P—Si bond angles in **I** fall in the  $108.5(1)$ - $109.3(1)^\circ$  range, while those of Al—As—Si in **III** have values between  $108.2(1)^\circ$  to  $109.6(1)^\circ$ . Correspondingly, the range of Si—P—Si is  $109.2(2)$  -  $110.5(1)^\circ$  and for **III**, Si—As—Si angles are  $109.0(1)$ - $110.4(1)^\circ$ . The geometries around the Al and P centers in compound **II** show a great similarity to those of **I** and **III**, despite the difference in the covalent radii of Cl and Br (0.99 and 1.14 Å, respectively). The average P—Al—Br bond angle is  $108.6(2)^\circ$ , and the average Br—Al—Br angle is  $110.4(2)^\circ$ , putting the Al atom in a slightly-distorted tetrahedral environment. The same is true for the

coordination sphere around the P atom in compound **II**, which has an average Al—P—Si bond angle of  $109.2(2)^\circ$  and an average Si—P—Si angle of  $109.8(2)^\circ$ .

The solvated nature of adducts **I** and **II** is of great interest in itself. As is the case with the As analog **III**, in both **I** and **II**, each adduct molecule is associated with, rather than bonded to, one solvate molecule. This becomes more clear upon viewing the unit cell of **II** (Fig. 3), in which the toluene molecules are aligned in the "channels" between rows of adduct molecules, such that **I-III** are "interstitially" solvated. The nature of the interaction between each monomer and toluene allows for facile drying of these compounds by evacuation of the solvates at room temperature for 30 min. to 1 h, after which the colourless crystals crumble to yield a white crystalline powder. Although the solvated crystals might be considered fragile, the desolvated solids of **I** and **II** exhibit extreme thermal stability, neither melting up to  $300^\circ\text{C}$  (the maximum limit of the melting point apparatus). The fortitude of these compounds during heating might be better understood by examining the nature of the aluminum-phosphorus bonds in **I** and **II**.

The essentially equal Al—P bond distances in **I** and **II** [ $2.392(4)$  Å and  $2.391(6)$  Å, respectively] are, to our knowledge, the shortest ever reported for aluminum-phosphorus molecular species. They are considerably shorter than those Al—P bonds found in previously reported Al-P adducts, whose corresponding lengths range from  $2.435(3)$  to  $2.585(2)$  Å.<sup>15,26-32</sup> The only shorter Al—P bond is in crystalline aluminum phosphide ( $2.367$  Å).<sup>33</sup> Although the Al—P bonds in **I** and **II** are dative bonds in that they are formed by the donation of a lone pair of electrons on the P atom to a vacant orbital on the Al atom, they are significantly shorter than the mean standard value of a dative aluminum-phosphorus bond ( $\text{Al}\leftarrow\text{P} = 2.54$  Å), as determined by Haaland in ref 34. At the same time, these bonds are also much longer than the length that is predicted by the modified Schomaker-Stevens rule for a normal Al—P bond ( $2.31$  Å).<sup>35</sup> Therefore, the Al—P bonds in compounds **I** and **II** demonstrate both normal and dative bonding character. The same has been said of the notably short Al—P bonds in the

aluminaphosphacubane,  $[i\text{-BuAlP}(\text{SiPh}_3)]_4$  (IV), reported by Cowley *et al.*,<sup>36</sup> which range from 2.409(4) to 2.417 Å.<sup>34</sup> The combination of normal and dative bonding between the aluminum and phosphorus centers in I and II that strengthens the Al—P bonds and greatly contributes to the stability of the desolvated adducts.

The extreme shortness of the Al—P bonds in I and II can be attributed to two additional factors. The first and most important of these being the high degree of electronegativity in the halogen atoms bonded to the Al center, which tremendously increases the Lewis acidity of the aluminum moieties. The second factor is the increased Lewis basicity of the  $\text{P}(\text{SiMe}_3)_3$  electron-donor species compared to other  $\text{PR}_3$  (R = alkyl, aryl) compounds due to the presence of the more electropositive Si atom. However, there may be  $p\pi\text{--}d\pi$  bonding between the P and the Si atoms, which would tend to counter this effect. Until now, the shortest reported Al—P bond length for an Al-P adduct was 2.435(3) Å in  $\text{Et}(\text{Cl})_2\text{Al}\cdot\text{P}(\text{SiMe}_3)_3$ .<sup>15</sup> Replacing the ethyl group on the Al center with a more electronegative halogen atom results in the formation of a stronger Lewis acid moiety,  $\text{AlX}_3$  (X = Cl, Br), and shortening of the Al—P bond by 0.044 Å. It is interesting to note that the difference in electronegativities between the Cl and Br atoms on the Al moieties in I and II, respectively, has essentially no effect on the Al—P bond lengths in these compounds [2.392(4) Å vs. 2.391(6) Å]. Likewise, the bond distance between the Al and P centers is unaffected by the difference between the steric bulk of the Cl substituents and that of the Br atoms. Although this might seem surprising at first, previous studies comparing the dissociation enthalpies of Al-N adducts with the same electron-donating species have shown that dative bonds to  $\text{AlCl}_3$  and  $\text{AlBr}_3$  are invariant in strength.<sup>34</sup> These investigations also revealed that such bonds to  $\text{AlCl}_3$  and  $\text{AlBr}_3$  are both 50% stronger than analogous bonds to  $\text{Me}_3\text{Al}$ . Thus, the bond-shortening effect appears to be more dependent upon the presence of the more electronegative halogen substituents on the Al centers in I and II, but not on the particular halogen itself.

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### Figure Captions

**Fig. 1.** ORTEP diagram (50% probability ellipsoids) showing the crystallographic atom numbering scheme and solid-state conformation of  $\text{Cl}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$  (I); hydrogen atoms have been omitted for clarity.

**Fig. 2.** ORTEP diagram (50% probability ellipsoids) showing the crystallographic atom numbering scheme and solid-state conformation of  $\text{Br}_3(\text{Cl})\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$  (II); hydrogen atoms have been omitted for clarity.

**Fig 3.** Projection diagram showing the unit cell in crystals of  $\text{Br}_3(\text{Cl})\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$  (II); hydrogen atoms have been omitted for clarity.

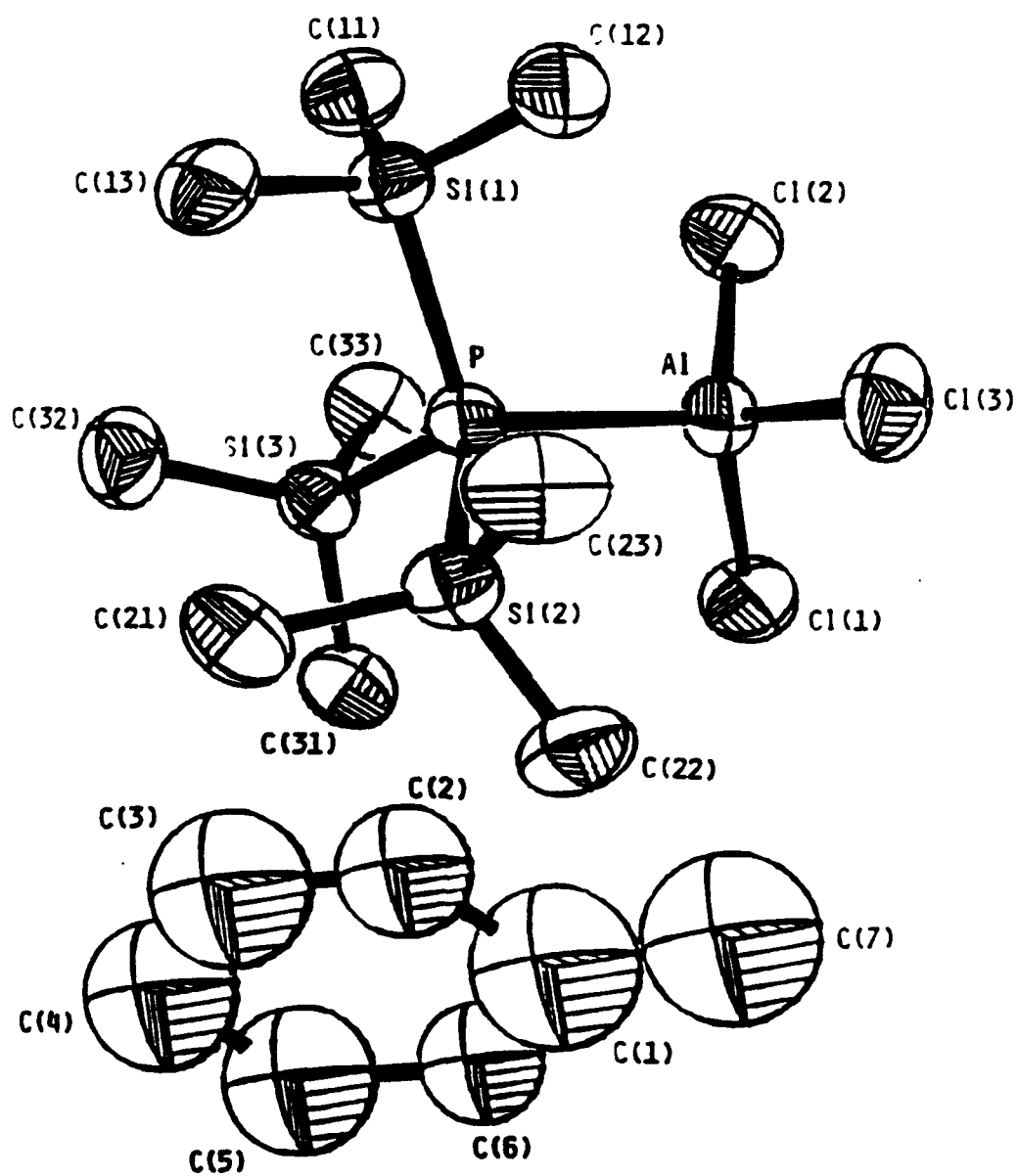


Fig. 1

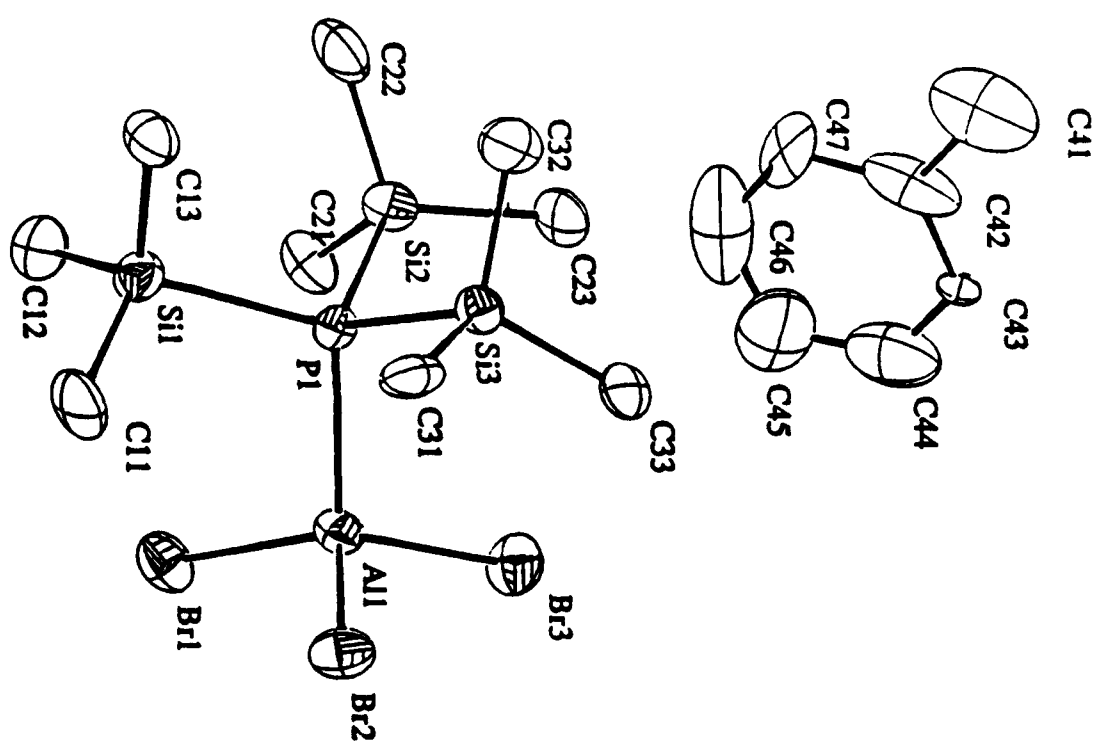


Fig. 2

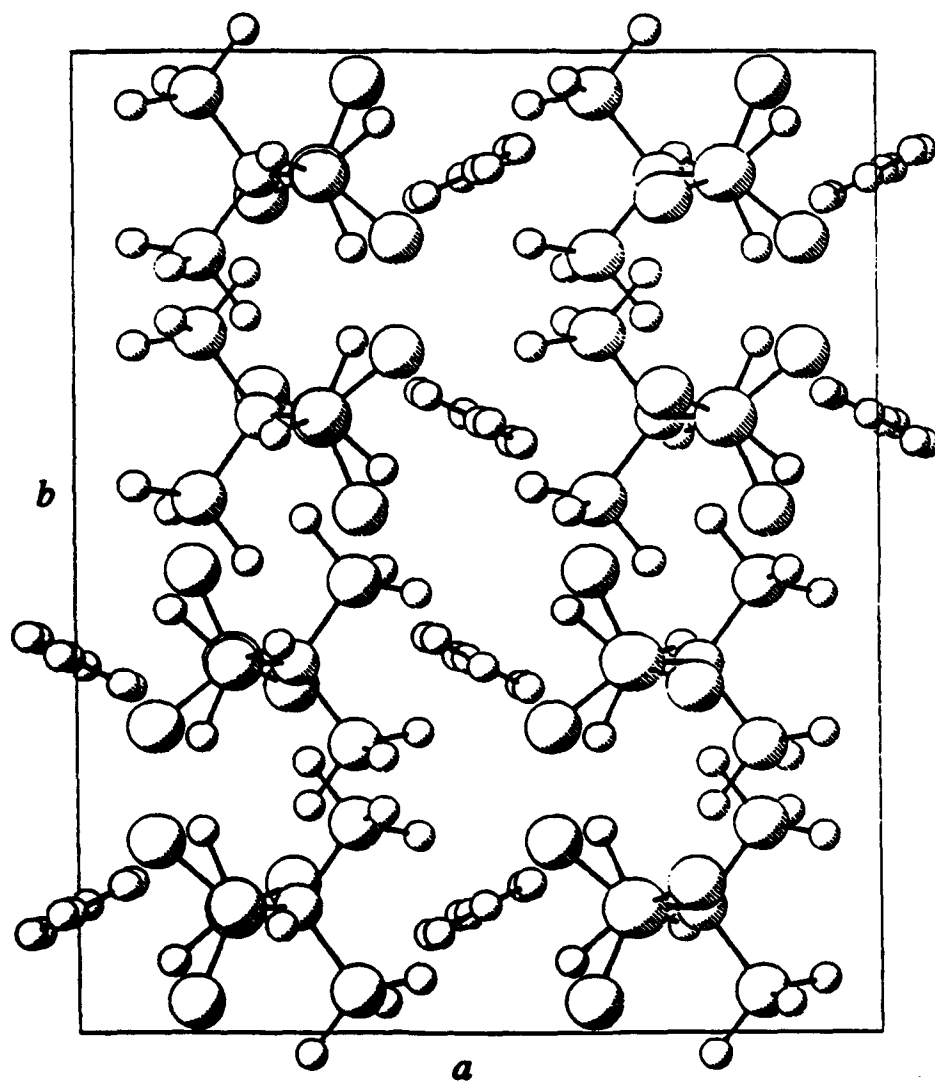


Fig. 3

Table 1. Crystallographic data and summary of data collection and refinement for  
 $\text{Cl}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$  (I) and  $\text{Br}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$  (II)

	I	II
Molecular formula	$\text{C}_9\text{H}_{27}\text{AlCl}_3\text{PSi}_3\cdot\text{C}_7\text{H}_8$	$\text{C}_9\text{H}_{27}\text{AlBr}_3\text{PSi}_3\cdot\text{C}_7\text{H}_8$
Formula weight	476.03	609.37
Crystal system	orthorhombic	orthorhombic
Space group	$Pbca(D_{2h}^{15})$ -No.61	$Pbca(D_{2h}^{15})$ -No.61
$a$ (Å)	17.501(2)	17.475(3)
$b$ (Å)	22.401(2)	22.468(4)
$c$ (Å)	13.799(2)	13.842(2)
$V$ (Å <sup>3</sup> )	5410(2)	5435(2)
$Z$	8	8
$D_{\text{calcd}}$ (g cm <sup>-3</sup> )	1.169	1.489
Temperature (K)	298	102
Crystal dimensions (mm)	0.20 x 0.30 x 0.70	0.35 x 0.30 x 0.30
$T_{\text{max}}:T_{\text{min}}$	1.00:0.60 (relative)	0.276:0.201
Radiation (wavelength)	Cu-K $\alpha$ (1.5418 Å)	Mo-K $\alpha$ (0.71073 Å)
$\mu$ (cm <sup>-1</sup> )	53.3	46.3
Scan type	$\omega$ -2 $\theta$	$\omega$
Scan width (°)	$0.60 + 0.14\tan\theta$	$1.00 + 0.70\tan\theta$
$\theta_{\text{max}}$ (°)	67	45
Intensity control reflections	3 3 1, 2 2 2, 6 4 3, 1 2 4;	8 0 0, 0 12 0, 008
Variation; repeat time	<2% ; 2 h	<1.5%; 100 reflections
No. of reflections recorded	4807(+ $h$ ,+ $k$ ,+ $l$ )	3808 (+ $h$ ,+ $k$ ,+ $l$ )
$R_{\text{merge}}$ , on No. of non-equivalent reflections	4807	3566

Table 1 (continued)

	I	II
<i>R</i> (merge)	-	0.066
No. of reflections retained, $I > 3.0\sigma(I)$	1674	-
No. of reflections retained, $I > 2.5\sigma(I)$	-	1522
No. of parameters refined	183	217
Extinction correction	$1.9(4) \times 10^{-7}$	-
<i>R</i> (F), <i>R</i> <sub>w</sub> (F) <sup>a</sup>	0.061 (0.088)	0.052 (0.050)
Goodness-of-fit <sup>b</sup>	1.82	1.09
Max shift; e.s.d. in final least-squares cycle	0.04	0.02
Final $\Delta\rho$ (e Å <sup>-3</sup> ) max.; min.	0.77; -0.47	0.64; -0.69

<sup>a</sup> $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ;  $R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}$ ;  $\sum w\Delta^2$  [ $w = 1/\sigma^2(|F_o|)$ ],  $\Delta = (|F_o| - |F_c|)$  was minimized.

<sup>b</sup>Goodness-of-fit =  $[\sum w\Delta^2 / (N_{\text{obs}} - N_{\text{para}})]^{1/2}$

Table 2. Selected bond lengths (Å) and angles (°), with e.s.d.s in parentheses, for  $\text{Cl}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$  (I) and  $\text{Br}_3\text{Al}\cdot\text{P}(\text{SiMe}_3)_3\cdot\text{C}_7\text{H}_8$  (II)

	I (X = Cl)	II (X = Br)
(a) Bond Lengths		
P—Al	2.392(4)	2.391(6)
P—Si(1)	2.299(3)	2.297(5)
P—Si(2)	2.300(3)	2.300(5)
P—Si(3)	2.286(4)	2.302(6)
Al—X(1)	2.125(4)	2.287(5)
Al—X(2)	2.118(3)	2.290(5)
Al—X(3)	2.112(4)	2.288(5)
(b) Bond Angles		
Al—P—Si(1)	109.3(1)	109.8(2)
Al—P—Si(2)	109.3(2)	109.6(2)
Al—P—Si(3)	108.5(1)	108.1(2)
Si(1)—P—Si(2)	110.5(1)	110.0(2)
Si(1)—P—Si(3)	110.0(1)	109.4(2)
Si(2)—P—Si(3)	109.2(2)	109.9(2)
P—Al—X(1)	107.8(1)	108.5(2)
P—Al—X(2)	108.1(1)	108.2(2)
P—Al—X(3)	108.4(2)	109.0(2)
X(1)—Al—X(2)	110.5(2)	111.1(2)
X(1)—Al—X(3)	111.4(2)	110.2(2)

Table 2 (continued)

	I (X = Cl)	II (X = Br)
(b) Bond Angles		
X(2)—Al—X(3)	110.6(2)	109.8(2)
P—Si(1)—C(11)	108.1(4)	107.9(5)
P—Si(1)—C(12)	107.1(4)	108.3(5)
P—Si(1)—C(13)	108.8(4)	108.5(5)
P—Si(2)—C(21)	109.2(3)	107.1(5)
P—Si(2)—C(22)	107.4(3)	108.7(5)
P—Si(2)—C(23)	108.1(4)	107.7(5)
P—Si(3)—C(31)	107.9(4)	108.2(5)
P—Si(3)—C(32)	109.2(4)	108.1(5)
P—Si(3)—C(33)	107.6(4)	107.6(5)